

THE COMPOSITION AND DETERMINATION OF
CERIUM OXALATE.

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THE salts of cerium appear to have been first brought to notice as medicinal agents in 1854 by Sir James Y. Simpson ("Note on the therapeutic action of salts of cerium," in the *Lond. and Edin. Monthly J.*, 1854, 564), who recommended the use of the nitrate, and about five years later the oxalate (*Med. Times and Gaz.* **19**, 280), which has since been chiefly employed. Cerium oxalate was recognised by the British Pharmacopœia in 1867, by that of the United States in 1870, and it still maintains a place in the present editions of those works, as also in the Pharmacopœias of several other countries.

Apart from the use of this salt in medicine, cerium has become of considerable importance during the past few years on account of the technical uses of the nitrate, since a mixture of one part of the latter with 99 parts of thorium nitrate constitutes the preparation employed for impregnating the familiar incandescent gas mantles. This application of cerium has given an impulse to the development or perfection of methods for its separation from the earths with which it occurs associated, especially lanthanum and didymium, and, while thus materially extending our knowledge of these elements, it has also practically created a new branch of chemical industry (compare "Contributions to the chemistry of Cerium," by L. M. Dennis and W. H. Magee, in *J. Amer. Chem. Soc.* 1894, 649—664, and especially "Beiträge zur Kenntniss der Ceriterden," by Otto N. Witt and Walter Theel, *Ber.* 1900, 1315—1324).

The cerium compounds were formerly obtained chiefly from cerite, which occurs in considerable amounts in Sweden, and affords at least 50 per cent. of cerium oxide. The thorium salts were obtained from the mineral thorite, which is found in Norway, and contains about 60—70 per cent. of its peculiar earth. According to Prof. O. N. Witt (*loc. cit.*), of the Charlottenburg Technical High School, who has given much attention to the technology of these rare earths, it was soon found that the supplies of thorite were not sufficient to even approximately meet the demand for thorium salts required for the incandescent gas-mantle industry.

A new source of supply was therefore sought for, and this has been found in the mineral monazite, which occurs in considerable quantities in North Carolina and in the Province of Bahia, in Brazil. It is from the latter source that the German industries now chiefly draw their supplies. Monazite is a cerous phosphate, in which a portion of the cerium is replaced by the other cerite earths. The thórium earth is not an integral constituent of the mineral, and, although quite regularly admixed with it, its amount varies within very broad limits. It is further stated by Witt that the monazite from Bahia contains at the most from 5—6 per cent. of thorium earth, while the earths of the cerite group amount to 50—60 per cent. or more, of which about one-half is cerium itself. The occurrence of these two earths in nature is therefore in inverse proportion to the requirements for industrial purposes. As enormous quantities of monazite have to be worked up in order to obtain the necessary supplies of thorium salts, and as only a very small proportion of the cerite earths which are obtained at the same time can be utilised in the form of cerium nitrate, it is evident that these must accumulate in considerable amounts. It has thus become an important problem, upon which technical chemists have been engaged for some time, to devise a practical method for the separation of the cerite earths, with the hope that they might then find some industrial applications for which the complex mixtures now available are not adapted. From the existing conditions of this industry, as briefly outlined, it may be inferred that the cerium oxalate of commerce, which, although used medicinally, likewise consists of such a complex mixture of the oxalates of cerium, lanthanum, and didymium, is at present more or less a by-product in the manufacture of thorium salts.

The importance which these rare earths have attained in recent years has not only led to an improvement in the processes for their technical separation, but has also resulted in the perfection of methods for their quantitative determination. We have, therefore, thought it desirable to compare the more recently proposed methods for the determination of cerium, more especially for the purpose of ascertaining the character of the cerium oxalate which is now supplied for medicinal purposes. In the course of our investigations, however, some other points of interest have incidentally been observed.

A careful review of the literature has served to reveal the fact that very little information concerning the determination of cerium is as yet to be found in the textbooks, and the analytical methods of special value are indeed of such recent date as only to be found in the current periodicals,

Even the latest edition of Fresenius' Quantitative Analysis that we have been able to consult contains no reference whatever to cerium. In Mohr's "Titrimethode," fifth edition, 1877, a short paragraph is devoted to the subject, and although it is stated that the oxide obtained by the ignition of the oxalate is readily decomposed by hydriodic acid with liberation of iodine, and that therefore one can make use in its analysis of the digestion method with potassium iodide and hydrochloric acid, no details of analysis are given. The oxide obtained on ignition was at that time regarded as ceroso-ceric oxide, Ce_3O_4 , and the atomic weight of cerium, as determined by Bunsen, was accepted as 46, whereas it had been formerly regarded as 58.216.

In Sutton's Volumetric Analysis, fourth edition, 1882, the estimation of cerium is referred to in a few lines, with the statement that "the most exact method of estimating this metal is by precipitating as cerous oxalate, then drying the precipitate, and strongly igniting in an open crucible, so as to convert it into ceric oxide." This method, however, would be of no value when lanthanum and didymium are present, as is usually the case, since they both form insoluble oxalates. The only further information given in the same work is as follows:—"Stolba (Zeits. für angew. Chem. 19, 194) states that the moist oxalate may be titrated precisely as in the case of calcic oxalate with permanganate, and with accurate results." It is obvious that this method is also only of value when no other oxalate than that of cerium is present, and it therefore would not be applicable to the commercial salt.

In the British Pharmacopœia of 1885, which was official until two years ago, the formula of cerium oxalate was given as $\text{CeC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$, in which it will be observed that cerium was regarded as bivalent in the cerous compounds.

The composition of cerium oxalate is at present generally represented by the formula $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$, as the element is now known to be trivalent in the cerous, and quadrivalent in the ceric salts. This formula is given by Beilstein (Handbuch der org. Chemie, 3rd edit. 1, 642), and it has been adopted by the Pharmacopœias and other standard works. It appears to have been originally proposed by Jolin (Bull. Soc. Chim. 1874, 21, 540), who has given brief descriptions of a large number of cerium salts, stated to have been prepared "from the pure oxide of cerium which had been obtained by the method of Mosander by treating the mixed hydrated oxides of cerium with chlorine." On consulting the original paper of Jolin, it is found, however, that the only evidence recorded for the proposed formula is that the salt loses $7\frac{1}{2}$ molecules of water at

100° C. (found 19·14 per cent., calculated 19·23 per cent.), and also that it was found to contain 38·89 per cent. of cerium, calculated 39·31 per cent. The latter result agrees, however, closely with a salt containing 10 molecules of water, which requires 38·6 per cent. cerium.

In connection with the formula for cerium oxalate, Beilstein also refers to Erk (Zeits. für Chemie, N. F. 1871, 7, 111) abstracted in J. Chem. Soc. 24, 494. In his paper, Erk remarks that the amount of water in the salt has been variously determined by different investigators. Rammelsberg (Pogg. Ann. 108, 44), for example, determined the "carefully dried" cerium oxalate as $\text{CeC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$, and Kjerulf (Ann. Chem. Pharm. 87, 12) gave it the formula $\text{CeC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, although neither of them stated the temperature at which they dried the oxalate. Gibbs (Zeits. für Chemie, N.F. 1, 15) regarded the mixed oxalates of cerium, lanthanum, and didymium as corresponding to the formula $\text{CeC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$, and employed this formula in his quantitative determinations of cerium. Erk himself considered the air-dried salt to have the formula $\text{CeC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$, and that 3 molecules of water were lost at 100° C., while the last molecule could not be expelled without the decomposition of the salt. He also states that, in its composition and behaviour on heating, cerium oxalate corresponds entirely to didymium oxalate. In all of these formulas cerium was regarded as bivalent, and as Erk used the atomic weight of 89 for cerium, his formula would require to be multiplied by three in order to make it comparable with that now accepted for cerium oxalate. His formula would thus become $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 12\text{H}_2\text{O}$ where $\text{Ce} = 140$.

Brauner (Chem. News, 1895, 71, 284), whose excellent work on the rare earths is well known, refers indirectly to the estimation of the water in cerium oxalate for the purpose of checking other determinations, but he does not note the result of this estimation nor the formula for the salt. The Commission of the German Chemical Society have adopted the atomic weight of cerium as 140, which is in accordance with Brauner's investigations (*loc. cit.*), and this has been more recently confirmed by Muthmann (Ber. 1898, 31, 1835) for CeCl_3 by the ebullioscope method. We have employed this atomic weight for our calculations in the analysis of cerium oxalate.

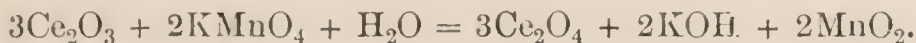
The views regarding the composition of cerium oxalate have been considered somewhat in detail, as they naturally have an important bearing upon the analysis of the salt, and especially, as we shall show later on, that we believe the accepted formula of the salt, with regard to the amount of water, to be not quite correct.

Methods for the Determination of Cerium.

Among the various methods that have been proposed for the determination of cerium, that of precipitating it by means of potash need not be considered, since lanthanum and didymium are precipitated by the same reagent.

About 40 years ago Bunsen (*Ann. Chem. Pharm.* **105**, 49) observed that the oxide obtained by the ignition of cerium oxalate might be estimated volumetrically by bringing it in contact with potassium iodide and strong hydrochloric acid, and determining the iodine set free.

Within the last few years two methods have been given for the determination of cerium in the presence of other metals. One of these is by Brauner (*Chem. News*, 1895, **71**, 285), and depends upon the oxidation of colourless cerous salts to yellow ceric salt by potassium permanganate



It is stated that in an acid solution the end of the reaction cannot be seen, on account of the deep yellow colour of the ceric salt formed, but that in alkaline solution the method gives excellent results.

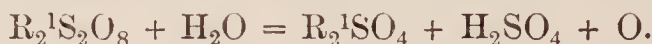
The other method of importance is one published by G. von Knorre in 1897 (*Zeits. für anorg. Chemie*, 1897, 685—688, and 717—725), abstracted in *Chem. Centralblatt* 1897, Bd. II. 1158, and 1898, Bd. I., 142. This method permits of the determination of cerium in the presence of thorium, lanthanum, didymium, and ferric salts. It depends upon the fact that yellow or orange coloured ceric compounds, in the presence of free acid, are reduced by hydrogen peroxide to colourless cerous compounds, the end of the reaction being recognised by complete decoloration—



In conducting the operation, a measured excess of hydrogen peroxide solution of known strength is added to an acidulated solution of a salt of ceric oxide, and, after complete decoloration, the excess of hydrogen peroxide is titrated back with potassium permanganate. Since 2 molecules KMnO_4 oxidise 10 atoms of Fe, or decompose 5 molecules of H_2O_2 , and furthermore as 1 molecule of H_2O_2 reduces 2 molecules of CeO_2 , it follows that 1 atom Fe corresponds exactly to 1 atom Ce or 1 molecule CeO_2 . If the substance contains a cerous salt, this must be first oxidised to the ceric condition, and in all reductions the liquid should be acidulated before the reducing agent is added. For the purpose of reduction a ferrous salt may be used in place of hydrogen peroxide, and with equally good results.

For the preliminary oxidation of the cerous salt Knorre found that neither the method of Gibbs with PbO_2 nor the electrolytic oxidation is quantitative. The treatment with MnO_2 in nitric acid solution is also not satisfactory, but on the contrary a reduction of the ceric salt takes place.

It was finally found that the oxidation of cerous to ceric salts is very conveniently effected by alkali persulphates, which, in slightly acid solution, decompose as follows:—



Even very dilute solutions of cerous salts, after acidulation with sulphuric acid, the addition of ammonium persulphate, and heating for a few minutes to boiling, become coloured yellow, and this is one of the sharpest reactions for the detection of cerium.

The conditions for the estimation of cerium by Knorre's method will be described more fully in the experimental part of our paper, and it may be noted that unless these conditions are carefully observed concordant results can not be obtained.

In the analysis of the oxalate, Knorre directs that it should be ignited, and the oxide dissolved in pure sulphuric acid, adding a little hydrogen peroxide if necessary, and heating on a sandbath till sulphuric acid vapours are given off. We have found it more expedient and quite as satisfactory to treat the oxalate directly with pure sulphuric acid.

Job (*Comptes rend.* Vol. 128, Jan. 29, 1899) abstracted in *Chem. News*, 79, (1899), 95, describes a method which is almost identical with that of Knorre's, except that he uses PbO_2 in nitric acid instead of ammonium persulphate, but, as has been previously shown by Knorre, this is unsatisfactory.

In 1898 P. Mengel published a paper on the "separation of cerium from lanthanum and didymium, and its estimation in the presence of the latter" (*Zeits. für anorg. Chemie* 1898, 19, 67—77), abstracted in *J. Chem. Soc.* 76, 1899, II., 223. According to his experiments "the estimation of cerium in admixture with lanthanum and didymium cannot be effected by determining the excess of oxygen in the precipitate obtained by means of sodium dioxide; the lanthanum and didymium oxides, when dried at 230°C ., still retain an excess of oxygen, and when the oxides are heated at 400°C ., the brown praseodidymium peroxide combines with the cerium dioxide and forms a compound which cannot be decomposed at a white heat. Consequently, the estimation of the peroxide oxygen by means of ferrous ammonium sulphate or potassium iodide gives results higher

than are required for the cerium dioxide. The same error is, of course, present when the oxides are obtained by heating a mixture of the oxalates, as in the analysis of commercial cerium oxalate. The estimation of cerium in the cerium earths by determining the peroxide oxygen in the ignited oxides also only gives accurate results when a very small quantity of praseodymium is present."

In 1899 Philip E. Browning published some important work "on the volumetric estimation of cerium" (*Amer. J. of Science* 1899, **8**, [48], and *Chem. News* 1900, **81**, 30 and 41). Browning determined the cerium in three specimens of pure cerium oxalate by a modification of Bunsen's method (*loc. cit.*), the details of which we shall refer to later on. Browning also refers to Stolba's method (*loc. cit.*), and although unable to find any subsequent confirmation of Stolba's statements, he was able to support them by his experiments.

From Browning's paper one would infer that the iodine method is only applicable for the analysis of pure cerium salts, and no reference is made therein to Knorre's work, which was published in 1897—1898. In the very valuable paper by Otto N. Witt and Walter Theel, previously referred to, which was published only a few weeks since, they speak of Knorre's method for the determination of cerium as an elegant one, and make use of ammonium persulphate for the technical separation of cerium from the accompanying earths.

Experimental.

For the purpose of our investigation the following three samples of cerium oxalate were employed:—

- I. Cerium oxalicum puriss., obtained from Germany.
- II. Cerium oxalicum venale, obtained from Germany.
- III. Cerium oxalate, supplied by a London firm of manufacturing chemists.

No. I. was quite white in appearance, and responded to all the ordinary qualitative tests for purity, with the exception of containing a slight trace of carbonate. The oxide obtained by ignition was of a pale yellow colour.

Nos. II. and III. represent the ordinary commercial salt employed for medicinal purposes, as supplied to the German and English markets. Both of them had a slight pinkish tint, and the residue left on ignition was of a brown colour, indicating the presence of didymium. No. II. contained traces of aluminium, iron, calcium, magnesium, and chloride with a distinct amount of phosphate. No. III. contained traces of aluminium, magnesium, and chloride.

With each of these specimens the following determinations were made :—

A. Examination of Cerium Oxalate.

1. The total amount of water.
2. The amount of oxide by ignition.
3. The amount of cerium by Brauner's method (only with No. 1).
4. The amount of cerium by von Knorre's method.
5. The amount of cerium by Browning's modification of Bunsen's method.
6. The amount of oxalic acid by titration with permanganate.

1. *Determination of the Water.*—It has been noted by previous investigators that the total amount of water in cerium oxalate cannot be expelled without the decomposition of the salt, and this is indicated by the following results. Specimens I. and III., representing a pure and a commercial salt respectively, were heated for some time in a water oven, but the weight did not become constant. At 130° C. the weight soon became quite constant, and the following figures were obtained :—

No.	Weight of Oxalate taken.	Loss at 130° C.	Percentage of Loss.
I.	0·8406	0·1786	21·25
III.	0·8722	0·1778	20·38

In consideration of the fact that the complete decomposition of cerium oxalate by strong ignition can only be attended by the elimination of carbon dioxide in addition to the water which it contains, we adopted a method for the estimation of the latter similar to that employed in ordinary organic combustions. A weighed quantity of the oxalate was placed in a platinum boat. The boat was inserted in a piece of hard glass tubing about 12 ins. long, one end of which was connected with the drying apparatus used for combustions, and to the other end a weighed absorption tube was attached containing pumice and sulphuric acid. Dry air was passed through the whole apparatus whilst the tube was heated by a Bunsen burner, the heat being first applied at the end nearest the drying apparatus, and gradually extended so that each part of the boat was heated to redness and no moisture was finally left in the tube. The results are given in the following table.

No.	Weight of Oxalate taken.	Weight of Water found.	Percentage of Water.	Calculated for $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$.
I.	0.5664 0.5234 0.6532	0.1432 0.1318 0.1642	25.28 25.18 25.14	24.87 per cent.
II.	1.1022	0.2736	24.83	Calculated for $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$.
III.	0.7703	0.1908	24.76	22.95 per cent.

These results are of considerable interest, inasmuch as they appear to prove quite conclusively that cerium oxalate contains 10 mols. of water, and not 9 mols., as is generally accepted. This conclusion is also substantiated by the weight of oxide obtained by ignition, and by the direct determination of the cerium in the salts.

2. *Determination of the Amount of Oxide by Ignition.*—For this purpose the oxalate was ignited in an open platinum crucible, heated to full redness in a Bunsen flame. The heating was repeated till the weight remained constant.

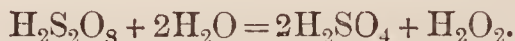
No.	Weight of Oxalate taken.	Weight of Oxide found.	Percentage of Oxide.	Calculated for $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$.	Colour of Oxide when Cold.
I. {	0.5964	0.2815	47.21	} 47.52	Very pale yellow.
II. {	0.5514	0.2613	47.13		Reddish-brown.
III. {	0.6358	0.3014	47.40		„
III.	0.5732	0.2672	46.61		

It will be seen that these results also correspond with the requirements for a salt containing 10 mols. of water.

3. *Determination of the Cerium by Brauner's Method.*—This was tried on the pure oxalate, but gave results about 10 per cent. below the calculated amount. The method appears to us to be an inconvenient one, owing to the formation of a bulky precipitate of hydrated oxides of manganese, which has to be filtered off through some inorganic medium.

4. *Determination of the Cerium by von Knorre's Method.*—About 0.5 gram. of the oxalate is gently heated on a sand bath in a porcelain dish, covered by a funnel, with 1 c.c. of pure sulphuric acid, till all effervescence has ceased. The residue is then completely washed into a conical flask, using about 100 c.c. of water. The solution should be perfectly clear, and on boiling no precipitate should separate out. If a precipitate does separate,

more acid should be added till it dissolves, but with the above proportions we found that the solution always remained clear on boiling. 4 grms. of ammonium persulphate are then dissolved in about 20 c.c. of cold water. The cerium solution is cooled to somewhat below 50°C ., about 10 c.c. of the persulphate solution are added, and the liquid again boiled for a minute or two. At this stage a precipitate often separates out, but it disappears as the oxidation proceeds. The liquid is again cooled to somewhat below 50°C ., 5 c.c. of the persulphate solution added, and again boiled. After cooling again, the last portion of the persulphate solution is added, and the liquid boiled for at least 15 minutes. 4 c.c. of sulphuric acid are now diluted with about 20 c.c. of water, and added to the hot liquid, which is again boiled for a minute or so. It is important to avoid the use of too much sulphuric acid in boiling with the persulphate solution, otherwise the ceric salt may become reduced through the formation of hydrogen peroxide—



The above acid solution of the ceric salt is now cooled to the room temperature, and diluted to about 100 c.c. or so, if necessary. A solution of ferrous sulphate (about 28 grms. of the crystallised salt dissolved in water, acidulated with H_2SO_4 , to 1 litre) standardised with potassium permanganate, is now run in till the deep yellow colour of the solution is completely discharged. The excess of ferrous sulphate is determined by adding N/10 permanganate till a pink tint is produced which remains permanent for more than a few seconds. The amount of ferrous sulphate used by the cerium is expressed in terms of N/10 solution. Since 1 litre of a decinormal cerium solution would contain 14.0 grms. of cerium, the percentage of cerium is given by the following formula :—

$$\frac{\text{No. of c.c. of N/10 FeSO}_4 \text{ used}}{\text{Weight of substance taken.}} \times 1.40.$$

The results of the analyses are given in the following table :—

No.	Weight of Oxalate taken.	No. of C.c. of N/10 FeSO_4 used.	Corresponding Percentage of Cerium.	Calculated Percentage of Cerium for $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$,
I. {	0.7180	19.65	38.32	} 38.68
	0.5333	14.60	38.33	
II. {	0.6506	7.82	16.83	
	0.8548	10.25	16.79	
III. {	0.6696	7.80	16.31	} 16.23
	0.6234	7.23	16.23	

The results obtained with pure cerium oxalate by this method serve to demonstrate its accuracy, and they also show that the specimens of commercial cerium oxalate examined contain but a little more than 40 per cent. of the pure salt, since the accuracy of the results is not influenced by the presence of lanthanum or didymium.

5. *Determination of the Cerium by Browning's Modification of Bunsen's Method.*—About 0.5 gm. of the oxalate was accurately weighed in an open platinum crucible, and heated in a Bunsen flame for 15 minutes. The oxide was then transferred to a 100 c.c. stoppered bottle, and 1 gm. of potassium iodide added, with a few drops of water. The air was displaced by passing a current of carbon dioxide into the bottle for a minute or so. If a pure oxide was being used, 5 c.c. of pure hydrochloric acid were added, and the bottle at once tightly stoppered; if brown oxides were used, the 5 c.c. of acid were diluted with an equal volume of water. The bottle was then placed on the top of the steam oven, and rotated from time to time till all the cerium dioxide had dissolved. This should be quite complete in half an hour. The bottle was allowed to cool, the contents diluted with about 50 c.c. of water, and titrated in the bottle with N/10 sodium thiosulphate, using starch as an indicator. From several blank experiments that were performed it was found that the iodine set free by the acid under these conditions was completely removed by the addition of a single drop of N/10 sodium thiosulphate, so that the error was small enough to be neglected. In some of the first experiments we performed, half a gramme of sodium bicarbonate was added to expel the air, and in this case also the error was negligible. For the calculation of the analyses the following formula may be employed:—

$$\frac{\text{No. of c.c. of N/10 sodium thiosulphate used}}{\text{Weight of substance taken}} \times 1.40.$$

The results of the analyses are given in the following table:—

No.	Weight of Oxalate taken.	No. of C.c. of N/10 $\text{Na}_2\text{S}_2\text{O}_3$ used.	Corresponding Percentage of Cerium.	Calculated Percentage of Cerium for $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$.
I. {	0.5544	15.32	38.68	38.68
	0.6152	17.00	38.68	
	0.4652	12.90	38.83	
	0.5998	16.65	38.86	
II. {	0.6358	8.40	18.50	}
	1.1022	14.50	18.42	
III.	0.5254	7.00	18.65	

It will be observed that by this method, the results obtained with pure cerium oxalate, agree very closely with those obtained by von Knorre's method, and are likewise exceedingly exact. With the commercial specimens, the percentages of cerium are found somewhat higher than by Knorre's method. This is probably due to the presence in them of some praseodidymium, which, as Mengel (*loc. cit.*) has shown, also forms a peroxide that liberates iodine from potassium iodide.

Although the iodine method is not an accurate one for the determination of cerium in the presence of praseodidymium, it affords some criterion as to the purity of an oxalate, and, when applicable, has the great advantage of simplicity over the more intricate persulphate method.

6. *Determination of the Oxalic radical in Cerium Oxalate by titration with Potassium Permanganate.*—About 0.2—0.3 grm. of the finely-powdered oxalate is weighed into a 200 c.c. conical flask. To this is added about 100 c.c. of water and 3 c.c. of pure sulphuric acid. The flask is heated on a water-bath, and the liquid, while hot, titrated with N/10 permanganate. The colour of the permanganate is discharged instantly so long as the oxalic acid is in excess, and the end of the reaction is marked by a pink tint which remains for about half a minute, but fades eventually to a pale yellow. As Knorre has pointed out (*Chem. Centralblatt.* 1897, B. II. 1158) the end of the reaction is sufficiently sharp as not to be disturbed by the observation of H. Rose, that permanganate in acid solution is decolorised by cerous compounds. The solution should be free from any undissolved portions of the oxalate.

For the calculation of the oxalic radical the following formula may be employed:

$$\frac{\text{No. of c.c. of N/10 permanganate used}}{\text{Weight of substance taken}} \times 0.44$$

The results of these determinations are given in the following table:—

No.	Weight of Oxalate taken.	No. of c.c. of N/10KMnO ₄ used.	Corresponding percentage of //C ₂ O ₄ .	Calculated "C ₂ O ₄ for Ce ₂ (C ₂ O ₄) ₃ .10H ₂ O.
				Per Cent.
I. {	0.1942	15.95	36.13	} 36.47
	0.3970	32.70	36.23	
II. {	0.4770	38.25	35.28	} 35.12
	0.2968	23.64	35.12	
III. {	0.2774	22.85	36.24	} 36.24
	0.3143	25.90	36.24	

It is evident that the above method is of quite limited value, for, as it only determines the oxalic radical, it gives no indication of the amount of cerium contained in the commercial mixed oxalates of cerium, lanthanum, and didymium.

In summarising the results of the analyses of pure cerium oxalate, the following comparisons of the two most important methods are obtained :—

Averages.		Averages.	Calculated for $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$.
	Per Cent.	(by iodine)	Per Cent.
Ce (by persulphate)	38·33	38·76	38·68
" C_2O_4 (by perman- ganate).	33·18	36·18	36·46
H_2O (by combus- tion).	25·20	25·20	24·86
	99·71	100·14	100·00

These results clearly show that the formula of cerium oxalate is $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$.

Lanthanum and Didymium Oxalates.

With regard to the composition of these salts, Beilstein (*loc. cit.*) records the following formulas :—

Lanthanum Oxalate, $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$, referring to Czudnowicz (Jahresbericht über die Fortschritte der Chemie, 1860, 128), which is an abstract of his paper in J. für prakt. Chemie, 80, 37, and to Clève (Bulletin 21, 202).

Didymium Oxalate, $\text{Di}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$, referring to Clève (Bulletin 21, 252).

Clève, however, does not state what method he employed to estimate the water in the two oxalates, which were dried over sulphuric acid.

Lanthanum oxalate, when ignited, affords a white oxide, La_2O_3 , of alkaline reaction, which dissolves readily in acids to form salts of the type LaR'_3 . It would not therefore, when pure, have any action upon potassium iodide and hydrochloric acid.

There are, however, two oxides of didymium formed by the ignition of its salts. According to Roscoe and Schorlemmer (German edit. 1887—1889, Vol. II., 365), didymium sesquioxide, Di_2O_3 , is obtained by the ignition of the hydroxide or a salt of a volatile acid. Didymium pentoxide, Di_2O_5 , is formed by heating the nitrate in a current of oxygen. It forms a brown porous mass, which, on strongly igniting decomposes into oxygen and the sesquioxide.

In order to verify the formulas assigned to the oxalates of lanthanum and didymium, and also to ascertain their influence on the previously described methods for the determination of cerium, specimens of the salts were prepared as follows: The pure carbonates were dissolved separately in a small quantity of hydrochloric acid, the solutions diluted, and precipitated with an excess of oxalic acid. The resulting oxalates were filtered off, washed till the washings were free from oxalic acid, and dried by exposure to the air. Lanthanum oxalate is quite white, but didymium oxalate has a distinct pinkish tint.

B. Examination of Lanthanum and Didymium Oxalates.

Both of these were examined according to the methods 1, 2, and 6, as described under cerium oxalate.

1. *Determination of the Water.*—The results of these determinations are given in the following table:—

Salt used.	Weight of Oxalate taken.	Weight of Water found.	Percentage of Water.	*Calculated for :
Lanthanum oxalate.	0.5794	0.1474	25.44	$\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ 25.00 per cent.
Didymium oxalate.	0.5890	0.1504	25.53	$\text{Di}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ 24.73 per cent.

2. *Determination of the Amount of Oxide by Ignition.*—0.5794 grm. of lanthanum oxalate gave 0.2582 grm. of oxide, or 44.57 per cent.

Calculated for $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ —45.00 per cent.

This oxide was of a pale cream colour. The amount of iodine liberated on treating it with potassium iodide and hydrochloric acid was equivalent to 0.35 e.e. N/10 thio sulphate.

0.5890 grm. of didymium oxalate gave 0.2678 grm. of oxide, or 45.47 per cent.

Calculated for $\text{Di}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ —45.60 per cent.

This oxide was of a chocolate-brown colour. The amount of iodine liberated on treating it with potassium iodide and hydrochloric acid was equivalent to 2.10 e.e. N/10 thiosulphate.

Both lanthanum and didymium are practically unacted upon by ammonium persulphate.

* In these calculations the atomic weight of lanthanum is taken as 138, and that of didymium as 142, the latter being the mean of the atomic weights of neo- and praseodidymium.

6. *Determination of the Oxalic Radical by Titration with Permanganate.*—The results of these determinations are given in the following table :—

Salt used.	Weight of Oxalate taken.	No. of c.c. of N/10 KMnO ₄ used.	Corresponding per-centage of "C ₂ O ₄ .	Calculated for
Lanthanum oxalate.	{ 0·2772	22·55	35·80 }	La ₂ (C ₂ O ₄) ₃ ·10H ₂ O,
	{ 0·3098	25·20	35·79 }	36·66 per cent.
Didymium oxalate.	{ 0·2644	21·50	35·77 }	Di ₂ (C ₂ O ₄) ₃ ·10H ₂ O,
	{ 0·2626	21·30	35·69 }	36·26 per cent.

The results of the preceding analyses, when summarised, may be briefly formulated as follows :—

Lanthanum Oxalate.—0·5794 gram. of the oxalate gave 0·2582 gram. of oxide. This, therefore, corresponds to—

$$\frac{25\cdot82}{0\cdot5794} \times \frac{276}{324} = 37\cdot97 \text{ per cent. La, since } \frac{\text{La}_2}{\text{La}_2\text{O}_3} = \frac{276}{324}.$$

—	Found.	Calculated for La ₂ (C ₂ O ₄) ₃ ·10H ₂ O.
	Per Cent.	Per Cent.
La	37·97	38·34
"C ₂ O ₄	35·80	36·66
H ₂ O	25·44	25·00
	99·21	100·00

Didymium Oxalate.—0·5890 gram. of the oxalate gave 0·2678 gram. of residue, which required 2·10 c.c. N/10 thiosulphate to combine with the liberated iodine. Since 1 c.c. N/10 thiosulphate = 0·0008 gram. O, 2·10 × 0·0008 = 0·0017, and this must be deducted from the weight of oxide found to convert it all into Di₂O₃, or 0·2678 — 0·0017 = 0·2661 gram. Di₂O₃. Hence the percentage of Di =

$$\frac{26\cdot61}{0\cdot5890} \times \frac{284}{332} = 38\cdot63 \text{ per cent.}$$

—	Found.	Calculated for Di ₂ (C ₂ O ₄) ₃ ·10H ₂ O.
	Per Cent.	Per Cent.
Di	38·63	39·01
"C ₂ O ₄	35·73	36·26
H ₂ O	25·53	24·73
	99·89	100·00

The facts here presented appear to us to demonstrate that both cerium oxalate and lanthanum oxalate contain ten molecules of water, and not nine molecules as at present accepted. With didymium oxalate, which has been correctly stated by Clève to contain ten molecules of water, these salts of the associated earths thus form a group analogous in composition, which may be represented by the general formula $R_2'''(C_2O_4)_3 \cdot 10H_2O$.

In connection with this investigation we may finally take the opportunity of outlining a plan for the more complete examination of commercial cerium oxalate, and, incidentally, of suggesting a few alterations in the text of the Pharmacopœia.

The British Pharmacopœia (edition of 1898) evidently intends to recognise the commercial cerium oxalate and not the pure salt, for it states that "it usually contains some lanthanum oxalate and didymium oxalate," and that "at a dull red heat it yields a reddish-brown powder," which of course reveals the presence of didymium. It may be safely stated that it always contains some lanthanum and didymium oxalates in varying amounts, but it is probably not generally known that these may constitute about 60 per cent. of its weight.

It is said to be "insoluble in water," but it is not perfectly insoluble, for Jolin (*loc. cit.*) has found that it is soluble in 8,175 parts of pure water, and in 375 parts of water containing 4 per cent. of sulphuric acid.

The statement that "when incinerated it loses 53 per cent. of its weight" is quite correct, but we may assume that this has been determined by experiment and not by calculation, since it corresponds with a salt containing ten molecules of water, whereas if the salt contained but nine molecules it would lose on incineration only 51.28 per cent. of its weight.

The statement of the Pharmacopœia that the residue obtained by ignition "dissolves without effervescence in boiling hydrochloric acid" is not quite correct, for some effervescence is produced owing to the liberation of chlorine. The test is probably intended for the detection of carbonates, but these may be best detected in the original salt, and if any carbonate were originally present as an impurity it would be likely to be completely decomposed at a red heat.

It may also be noted that the reaction depending upon the production of a crystalline precipitate in an acid solution by potassium sulphate, although applicable to the commercial oxalate, is not characteristic of cerium, for it is afforded as well by the oxalates of lanthanum and didymium. A really characteristic and exceedingly delicate test for cerium has

been observed by Knorre (*loc. cit.*), and we find that this may be practically formulated as follows :

If 0.1 gramme of cerium oxalate be gently heated, in a test-tube, with 0.5 c.c. of pure sulphuric acid till all effervescence ceases, the liquid diluted with 10 c.c. of water and 1 gramme of ammonium persulphate dissolved in the cold liquid, on subsequently heating the liquid to boiling for a minute or so a bright yellow colour is produced. This reaction is so very delicate that we have thus been able to detect traces of cerium in the pure oxalates of lanthanum and didymium.

While the presence of didymium in cerium oxalate may be readily recognised by the reddish-brown colour of the residue left on ignition, the presence of lanthanum will also be indicated by the alkaline reaction of the residue to litmus, provided that the alkaline earths, calcium, etc., are found to be absent.

For conducting the ordinary qualitative tests, the salt may be dissolved in dilute hydrochloric acid, when no effervescence should occur, showing absence of carbonates, and the solution should give no coloration with hydrogen sulphide, showing absence of the heavy metals. The salt dissolved in dilute nitric acid may be tested in the usual way for iron, chlorides, sulphates, and phosphates, the latter with ammonium molybdate. If the salt be boiled with solution of potassium hydrate and filtered, one portion of the filtrate may be tested with ammonium chloride for aluminium, and another portion with ammonium sulphide for zinc. If the salt be heated with a little pure sulphuric acid till all effervescence ceases, then diluted with water, a slight excess of ammonia added, and again heated to boiling, the filtrate may be tested with sodium phosphate for magnesium. The alkali and alkaline earth metals may be detected by the flame test after moistening the salt with hydrochloric acid.

In addition to these tests a more complete examination may include (1) the determination of the residue left on ignition, (2) the quantitative estimation of the cerium by the persulphate or the iodine methods, and (3) of the oxalic acid by titration with decinormal potassium permanganate.

In view of the complex character of commercial cerium oxalate, and the tendency of modern medicine to employ pure substances of a definite composition, the question naturally suggests itself whether the pure salt would not be more suitable for medicinal purposes. It is important, however, to consider in this connection that the original observations which led to the introduction of cerium oxalate as a therapeutic agent were based upon the use of the commercial salt, and even at the present time pure cerium oxalate possesses a market value which is about fifty times

that of the preparation recognised by the Pharmacopœia. Lanthanum and didymium oxalates command such a very high price as to quite preclude their use in medicine. It is possible that all of these salts possess similar therapeutic properties (compare Pharm. Journ. May, 1877 p. 909), but it is nevertheless desirable that pure cerium oxalate should be subjected to therapeutic tests, as by comparison with the known effects of the mixed oxalates as they exist in the commercial salt the action of lanthanum and didymium oxalates might thus be indirectly determined.
